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(54) Aluminum hydroxide, method for producing the same, and use of the same

Aluminiumhydroxid. Verfahren zur Herstellung und Verwendung davon

Hydroxyde d'aluminium, procédé de sa production et son utilisation

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Description

[0001] The present invention relates to an aluminum hydroxide, a method for producing the same, a use of the same, and a rubber composition for tire tread using the same. More particularly, it relates to an aluminum hydroxide which

5 can be applied to various uses such as fillers for paint, synthetic resin, adhesive or paper, and agent for paper making/painting, in addition to a main use such as rubber filler, a method for producing the same, a method of using the same, comprising containing the same in a rubber, a method for using the same as a filler in a rubber composition for tire tread, and a rubber composition for tire tread using the same.

[0002] As a rubber reinforcing filler, a carbon black is generally used. When using a rubber containing the carbon 10 black for a tire tread, there arises a problem that the rolling resistance is increased and the fuel consumption is increased.

[0003] On the other hand, with the improvement of the performance of automobiles, the grip performance required to a tire has been becoming more severe. As a conventional technique for solving these problems, it is known to use silica (white carbon) as a filler.

15 [0004] However, when silica is used as a filler, the problem arises that the reduction of the rolling resistance, and grip performance are not sufficient and the viscosity of the rubber and silica at the time of kneading is high and, furthermore, the processability is insufficient, resulting in deterioration of the productivity.

[0005] An object of the present invention is to provide an aluminum hydroxide which can be used as a filler which 20 can improve the processability and productivity at the time of kneading with a rubber for tire tread while a sufficient reinforcing effect such as the sufficient grip performance and the sufficient rolling resistance reduction effect is imparted to the rubber for tire tread in case of filling in the rubber for tire tread.

[0006] Under these circumstances, the present inventors have intensively studied so as to accomplish the above 25 object. As a result, it has been found that an aluminum hydroxide having a specific particle size, a specific BET specific surface area and a specific pore size can be used as a filler which satisfies the above object in whole or in part. It has also been found that this aluminum hydroxide can be obtained by mixing and neutralizing a basic solution and an acidic 30 solution, one or both of the solutions containing an aluminum ion, under high-speed rotary shear stirring which produces a shear rate of not less than 1000 sec⁻¹. Thus, the present invention has been accomplished.

[0007] The present invention provides an aluminum hydroxide wherein the mean particle size of the secondary particles is from 0.1 to 8 µm, the BET specific surface area is not less than about 30 m²/g and the pore size distribution 35 has a maximum value within the range from 5 to 100 nm.

[0008] The present invention also provides a method for producing an aluminum hydroxide wherein the mean particle size of the secondary particles is from 0.1 to 8 µm, the BET specific surface area is not less than about 30 m²/g and the pore size distribution has a maximum value within the range from 5 to 100 nm, which comprises carrying out a neutralization reaction by mixing a basic solution and an acidic solution, one or both of the solutions containing an 40 aluminum ion, under high-speed rotary shear stirring which produces a shear rate of not less than 1000 sec⁻¹, and separating the resulting neutralization reaction product, followed by drying using a flash dryer, a hot-air transfer type dryer or a vacuum dryer. The neutralization reaction product may be washed prior to drying.

[0009] The present invention also provides the use of an aluminum hydroxide wherein the mean particle size of the 45 secondary particles is from 0.1 to 8 µm, the BET specific surface area is not less than about 30 m²/g and the pore size distribution has a maximum value within the range from 5 to 100 nm in a rubber composition, for example as a filler in a rubber composition for tire tread.

[0010] The present invention also provides a rubber composition for tire tread, comprising a rubber component and an aluminum hydroxide wherein the mean particle size of the secondary particles is from 0.1 to 8 µm, the BET specific surface area is not less than about 30 m²/g and the pore size distribution has a maximum value within the range from 5 to 100 nm, the aluminum hydroxide being present in the composition in a proportion of 10 to 200 parts by weight 50 based on 100 parts by weight of the rubber component.

[0011] Regarding the aluminum hydroxide of the present invention, the mean particle size of the secondary particles is from 0.1 to 8 µm, the BET specific surface area is not less than about 30 m²/g and the pore size distribution has a maximum value within the range from 5 to 100 nm. For example, the aluminum hydroxide may be used as a filler in a tire tread rubber.

[0012] It is necessary that the BET specific surface area of the aluminum hydroxide of the present invention is not less than about 30 m²/g, preferably from 30 to 500 m²/g, more preferably from 50 to 350 m²/g. When the BET specific surface area of the aluminum hydroxide is less than about 30 m²/g, the reinforcing effect to the rubber is not obtained. On the other hand, the larger the BET specific surface area of the aluminum hydroxide becomes, the larger the reinforcing effect to the rubber. However, when it exceeds 350 m²/g, the dispersion properties of the aluminum hydroxide are slightly deteriorated and the strength of the filled rubber is slightly lowered.

[0013] In the aluminum hydroxide of the present invention, the maximum value of the pore size distribution is within 55 the range from 5 to 100 nm, preferably from 8 to 80 nm. The maximum value of the pore size distribution refers to a

maximum value in an index pore size volume distribution chart measured by a mercury porosimeter method or an N_2 adsorption method. The maximum value of the pore size distribution within the range from about 5 to 100 nm is not necessarily the largest maximum value in the pore size distribution, and the aluminum hydroxide of the present invention may have another maximum value in addition to that within the range from 5 to 100 nm. But when the pore size distribution only has a maximum value within the range less than 5 nm or the range more than 100 nm, the desired reinforcing effect to the rubber is not obtained.

[0014] The mean particle size of the secondary particle of the aluminum hydroxide of the present invention is within the range from 0.1 to 8 μm , preferably from 0.1 to 5 μm . In the present invention, the mean particle size of the secondary particles may be measured under the conditions that the measuring mode is a centrifugal sedimentation mode in which the rotating mode is acceleration rotation at 240 rpm/min, using a centrifugal sedimentation type particle size distribution measuring device, Model SA-CP3 (manufactured by Shimadzu Co.). A measuring solution may be prepared by suspending the aluminum hydroxide to be measured in an aqueous 0.2 wt% sodium hexametaphosphate solution, followed by subjecting to an ultrasonic dispersion treatment for 10 minutes, and using the resulting solution for the measurement.

[0015] The primary particle size of the aluminum hydroxide of the present invention is preferably within the range from 10 to 100 nm. The primary particle size may be measured by using a field emission type scanning electron microscope, FE-SEM, Model S-4500 (manufactured by Hitachi Seisakusho Co.). The primary particle is the minimal unit of the particle and readily agglomerates into the secondary particle.

[0016] On the other hand, the aluminum hydroxide of the present invention may optionally be treated with various surface treating agents. The surface treating agent may be extremely effective means for improving the dispersion properties in case of mixing the aluminum hydroxide of the present invention with a resin matrix such as rubber, and improving the adhesion properties of the interface between the aluminum hydroxide and resin. Examples of the surface treating agent to be applied include known organic treating agent and inorganic dispersant. More specific examples thereof include various coupling agents, fatty acid metal salts, fatty acids and alcohols.

[0017] The aluminum hydroxide of the present invention can, for example, be obtained by mixing and neutralizing a basic solution and an acidic solution, one or both of the solutions containing an aluminum ion, under high-speed rotary shear stirring, filtering the resulting neutralization reaction product, followed by washing and further drying using a flash dryer, a hot-air transfer type dryer or a vacuum dryer.

[0018] In the present invention, high-speed rotary shear stirring refers to stirring due to the mechanical energy (e.g. shear force, variation in pressure, cavitation, collision force or potential core) produced between a high-speed rotating turbine or rotor at a circumferential speed of usually 1 to 40 m/sec and a stator or screen, using a stirrer such as a homomixer or homogenizer, that is, a stirrer comprising a high-speed rotating turbine or rotor, and a stator or screen provided on the peripheral part at a clearance of usually not more than 2 mm from the rotating part.

[0019] Examples of the high-speed rotary shear stirrer include T.K. Homomixer, T.K. Homomic inlineflow, Homojetter M (the above stirrers are manufactured by Tokushu Kika Kogyo Co., Ltd.), Cleamix (manufactured by M. Technic Co., Ltd.), Polytron homogenizer, Megatron homogenizer (manufactured by KINEMATICA Co.) and Supraton (manufactured by Tsukishima Kikai Co., Ltd.).

[0020] Regarding the conditions of these high-speed rotary shear stirrers, the shear rate can be represented by $x/y \times 10^3 \text{ sec}^{-1}$ wherein a circumferential speed of a high-speed rotating turbine or rotor is $x \text{ m/sec}$ and a clearance between the turbine or rotor and a stator or screen is $y \text{ mm}$.

[0021] The high-speed rotary shear stirring in the present invention refers to high-shear stirring capable of producing a shear rate of not less than 1000 sec^{-1} . When the shear rate is less than about 1000 sec^{-1} , mixing of two solutions, i.e. basic solution and acidic solution, and the effect of mechanical dispersion of the resulting aluminum hydroxide particle-containing slurry are insufficient so that a coarse agglomerate is liable to be formed.

[0022] Since the neutralization reaction between the basic solution and acidic solution takes place at a very fast rate, the aluminum hydroxide is momentarily deposited in the reaction. Therefore, when the neutralization reaction is conducted by using of typical screw type low-speed and moderate-speed rotary stirrers, a coarse agglomerate is liable to be formed. On the other hand, when the neutralization reaction between the basic solution and acidic solution is conducted under the high-speed rotary shear stirring, uniform mixing of two solutions is rapidly conducted. Therefore, generation of the coarse particles caused by local non-uniform mixing of the basic solution and acidic solution is reduced, and an ultrafine aluminum hydroxide can be obtained.

[0023] Examples of the device used in the reaction include batch device and continuous reaction device. The addition order of the solutions and time required for the addition are not specifically limited.

[0024] As the batch device, those comprising a tank as a reaction vessel, a high-speed rotary shear stirring device being provided in the tank, are generally used. When using the above device, it is possible to use a method of previously charging an alkali metal aluminate solution or an acidic solution in the reaction vessel and adding dropwise the acidic or basic solution under the high-speed rotary shear stirring, or a method of previously charging a dispersion medium such as water in the reaction vessel and simultaneously adding the basic and acidic solution to the dispersion medium under the high-speed rotary shear stirring. In case of the latter, there can also be used a method of previously adjusting

the pH of the dispersion medium to be charged in the reaction vessel to a predetermined value and adding the basic and acidic solutions while maintaining the pH.

[0025] Examples of the continuous device include tank continuous type device and pipeline continuous type device. The tank continuous type device is that comprising a tank equipped with a high-speed rotary shear device, and a method of continuously supplying the basic and acidic solutions in the tank and getting the deposited aluminum hydroxide together with the solution after the reaction through an outlet is used. The pipeline continuous type device is that comprising a high-speed rotary shear stirrer incorporated into a line, and a method of continuously supplying the basic and acidic solutions in the line is used.

[0026] In the present invention, the reaction temperature under the high-speed rotary shear stirring is preferably maintained at 0 to 50°C, more preferably 0 to 30°C. In the neutralization reaction of sodium aluminate, when the reaction temperature becomes higher, the crystal growth is remarkably accelerated and a particle having a large primary particle size is obtained. Therefore, when the reaction temperature becomes higher than 50°C, an aluminum hydroxide having a small specific surface area, wherein the primary particle is grown, is liable to be formed.

[0027] In the present invention, the degree of neutralization of the neutralization reaction is not specifically limited. It is possible to prepare under any condition such as condition of the excess acidic solution, neutral condition or condition of the excess basic solution. Any condition such as condition of the excess acidic solution, neutral condition or condition of the excess basic solution is selected according to the use of the resulting aluminum hydroxide.

[0028] The kind of the basic solution used in the neutralization reaction is not specifically limited.

[0029] Examples of the basic solution include the solution of sodium hydroxide, potassium hydroxide or aqueous ammonia, and examples of the basic solution containing an aluminum ion include the solution of an alkali metal aluminate such as sodium aluminate or potassium aluminate.

[0030] The concentration of the basic solution used is not specifically limited. For example, when using the alkali metal aluminate solution, the aluminum concentration of the basic solution is preferably from 5 to 400 g/l, more preferably from 15 to 250 g/l, in terms of Al_2O_3 . When using the sodium aluminate solution, the molar ratio of the Na_2O of the sodium aluminate solution to the Al_2O_3 is preferably within the range from 1.0 to 10, more preferably from 1.4 to 8.

[0031] When the aluminum concentration of the alkali metal aluminate solution is high, it is in the state where the particle growth rate is fast and the growth of agglomeration is accelerated. Therefore, it is liable to be impossible to obtain particles which are highly dispersed and contain no coarse particles. On the other hand, when the aluminum concentration of the alkali metal aluminate solution is low, the weight of the aluminum hydroxide to be deposited is low and the productivity is liable to be lowered.

[0032] Examples of the alkali metal aluminate solution include sodium aluminate solution and potassium aluminate solution. Among them, the sodium aluminate solution, which is generally used in the Bayer process of obtaining alumina from bauxite, is preferably used in view of the availability and economical efficiency.

[0033] On the other hand, the acidic solution is not specifically limited, and an inorganic or organic acid is used. Examples of the inorganic acid include sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, perchloric acid and boric acid, and examples of the organic acid include carboxylic acid such as formic acid, acetic acid or propionic acid; dicarboxylic acid such as oxalic acid; and hydroxycarboxylic acid such as gluconic acid.

[0034] As the acidic solution containing an aluminum ion, there can be used, for example, a solution of an inorganic salt such as aluminum sulfate or aluminum nitrate, or a solution of an organic salt such as aluminum acetate.

[0035] An aluminum hydroxide is deposited as the neutralization reaction product by subjecting the basic solution and acidic solution to the stirring, mixing and neutralizing treatments according to the above method. In the present invention, the aluminum hydroxide is obtained by solid-phase separation such as filtration, preferably washed, and then dried, using a flash dryer, a hot-air transfer type dryer or a vacuum dryer.

[0036] The dryer is generally classified into the following eight kinds based on the mechanism, i. e. (1) material standing type dryer, (2) material transfer type dryer, (3) material stirring type dryer, (4) hot-air transfer type dryer, (5) cylindrical dryer, (6) infrared dryer, (7) vacuum dryer and (8) high-frequency dryer (Chemical Engineering Handbook, Maruzen). The flash dryer is a dryer utilizing flash vaporization (self-vaporization), which is not within the range of a conventional dryer.

[0037] The flash dryer in the present invention is a dryer having such a construction that a solvent is evaporated by pressure-spraying a solution heated to the temperature higher than a boiling point at atmospheric pressure through an outlet, thereby obtaining a solid particle.

[0038] The hot-air transfer type dryer in the present invention refers to a dryer for drying a liquid-containing powder such as slurry in hot air at high temperature. Specifically, a fluidized bed dryer, an airborne dryer and a spray dryer correspond to the hot-air transfer type dryer. Examples of the fluidized bed dryer include slurry dryer, conduction flow (both dryers are manufactured by Okawara Seisakusho Co., Ltd.) and medium fluid dryer (manufactured by Nara Kikai Seisakusho Co., Ltd.). Examples of the airborne dryer include flash jet dryer (manufactured by Kurimoto Tekko Co., Ltd. and Seishin Kogyo Co., Ltd.). Examples of the spray dryer include Spray dryer (manufactured by Sakamoto Giken Co., Ltd., Nara Kikai Seisakusho Co., Ltd. and Okawara Kakoki Co., Ltd.) and Mobile minor (manufactured by Niro A/S).

[0039] Furthermore, the vacuum dryer is a device for drying by optionally cooling or heating a material to be dried under a vacuum atmosphere. Examples of the vacuum dryer include MZ processor, Belmax (both dryers are manufactured by Okawara Seisakusho Co., Ltd.), vacuum rotary dryer (manufactured by Tokuju Kosakusho Co., Ltd.) and Vacuum tumble dryer (manufactured by Kusunoki Seisakusho Co., Ltd.).

5 [0040] In the present invention, aging can be optionally conducted after the neutralization reaction. The crystal form and particle form of the aluminum hydroxide can be modified by aging. When the aluminum hydroxide after aging is used, for example, as a resin filler, it shows the improved dispersion and reinforcing properties in comparison with the case where the aluminum hydroxide before aging is used. The method of aging is not specifically limited, and examples thereof include a method of aging the neutralization reaction product immediately after depositing, and a method comprising separating the neutralization reaction product from the reaction solution and optionally washing the separated product, followed by immersing in a separately prepared solution to conduct aging. Examples of the aging conditions include condition of changing the temperature variously under a normal pressure and condition of conducting aging under elevated pressure. The aging is generally conducted by maintaining mixing at preferably 0 to 60°C under a normal pressure for preferably 30 minutes to one week.

10 [0041] In the present invention, a water-soluble polymer can also be allowed to coexist at the time of mixing under the high-speed rotary shear stirring. The water-soluble polymer is adsorbed on the surface of the deposited aluminum hydroxide particle to make particles repulse each other, thereby imparting the dispersion effect. As the water-soluble polymer, a polyacrylate is preferably used in an acidic to neutral solution and a polyacrylamide is preferably used in a neutral to basic solution.

15 [0042] In the present invention, the aluminum hydroxide may optionally be subjected to a grinding treatment. In this case, since the agglomerated particle can be nearly ground into a primary particle, better improving effect to dispersion properties can be obtained. The grinding may be carried out by using a known grinding device. In case of wet grinding, there can be used, for example, a Wet tower mill (manufactured by Kubota Co., Ltd.), Apex mill (manufactured by Kotobuki Giken Kogyo Co., Ltd.), Micros (manufactured by Nara Kikai Seisakusho Co., Ltd.), or Dyno-mill (manufactured by Kabushikikaisha Shinmaru enterprise). As a dry mill, there can be used, for example, Jet mills (manufactured by Seishin Kogyo, Nihon Newmatic Kogyo Co., Ltd. or Nisso Engineering Co., Ltd.), Current jet mill (manufactured by Nisshin Engineering Co., Ltd.), Counter jet mill (manufactured by Hosokawa Micron Co., Ltd.), Kolloplex (manufactured by Hosokawa Micron Co., Ltd.), pin mill, vibration mill, or ball mill.

20 [0043] The aluminum hydroxide of the present invention is preferably used in a rubber composition for tire tread. As a rubber component used in the rubber composition for tire tread, there can be used those which are known in the corresponding field, such as cis-1,4-polyisoprene, low cis-1,4-polybutadiene, ethylene-propylene-diene rubber, chloroprene, halogenated butyl rubber, acrylonitrile-butadiene rubber or natural rubber, in addition to styrene-butadiene rubber. The amount of the aluminum hydroxide added to the rubber component varies depending on the amount of the rubber component used as a raw material and other inorganic fillers used in combination, but the aluminum hydroxide is normally used in the amount within the range from 10 to 200 parts by weight based on 100 parts by weight of the rubber component. It is possible to optionally contain further components, such as inorganic fillers (e.g. carbon black, silica, talc or clay), process oils, silane coupling agents, vulcanization agents or antioxidants, in the rubber composition for tire tread, in addition to the aluminum hydroxide of the present invention.

25 [0044] The rubber composition for tire tread thus obtained can improve the grip performance and reduce the rolling resistance. Besides, the rubber composition has a small viscosity at the time of kneading the rubber with the aluminum hydroxide in comparison with the case of kneading the rubber with silica, and is also superior in processability.

30 [0045] As described hereinabove, the aluminum hydroxide of the present invention has a specific mean particle size of a secondary particle, a specific BET specific surface area and a specific pore size distribution, and has the following effect. That is, when the aluminum hydroxide of the present invention is used as a filler in a rubber composition for tire tread, the sufficient effect of improving the grip performance and reducing the rolling resistance is imparted to the rubber composition and, at the same time, the viscosity at the time of kneading the rubber with the aluminum hydroxide is reduced, thereby improving the processability and productivity. Thus, the industrial utilization value thereof is great.

35 [0046] The following Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof. In the present invention, powder physical properties and physical properties of the rubber-filled composition were measured in the following manner.

40 [0047] BET specific surface area: It was measured by a fluidized specific surface area automatic measuring device (manufactured by Shimadzu Co., trade name: Flow Soap II2300PC-1A).

45 [0048] Mean particle size of the secondary particles: It was measured under the conditions that the measuring mode is a centrifugal sedimentation mode in which the rotating mode is acceleration rotation at 240 rpm/min, using a centrifugal sedimentation type particle size distribution measuring device, Model SA-CP3 (manufactured by Shimadzu Co.). A measuring solution was prepared by suspending the aluminum hydroxide to be measured in an aqueous 0.2 wt% sodium hexametaphosphate solution, followed by subjecting to an ultrasonic dispersion treatment for 10 minutes, and using the resulting solution for the measurement.

[0049] Pore size: A value of less than 3.2 nm was measured by the N_2 adsorption method and that of not less than 3.2 nm was measured by the mercury porosimeter method (Autoscan 33 manufactured by Cantacrom Co.).

[0050] Grip performance: A tan δ -temperature dispersion curve was obtained by measuring under the conditions of a frequency of 10 Hz, an initial strain of 10%, an amplitude of $\pm 0.25\%$ and a heating rate of $2^\circ\text{C}/\text{minute}$ according to JIS K-6394, and a tan δ at 0°C in the dispersion curve was determined. Here, tan δ indicates a ratio of a storage elastic modulus G' to a loss elastic modulus G'' , i. e. G''/G' . The resulting measured value was indicated by a relative value in case of the measured value of the rubber-filled composition obtained in Comparative Example 1 being 100. The smaller this relative value, the better the grip performance is.

[0051] Rolling resistance: A tan δ at 60°C in the tan δ -temperature dispersion curve obtained under the above conditions according to JIS K-6394 was determined. The resulting measured value was indicated by a relative value in case of the measured value of the rubber-filled composition obtained in Comparative Example 1 being 100. The smaller this relative value, the lower the rolling resistance is.

[0052] Processability: In case of preparing a rubber composition containing an aluminum hydroxide, a torque obtained immediately before the completion of the kneading of the rubber and aluminum hydroxide was read, and the processability was evaluated from the resulting value. The resulting measured value was indicated by a relative value in case of the measured value of the rubber-filled composition obtained in Comparative Example 1 being 100. The smaller this relative value, the better the processability is.

Example 1

(Production of aluminum hydroxide)

[0053] To 1 liter of a sodium aluminate solution [sodium concentration: 125 g/l in terms of Na_2O , molar ratio $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 : 1.55$] as a basic solution in a stainless steel tank equipped with a baffle, 600 ml of an aqueous aluminum sulfate solution (aluminum concentration: 5.3% by weight in terms of Al_2O_3) as an acidic solution was added with icecooling under stirring under the conditions of a shear rate of 11000 sec^{-1} , using a Homomixer (manufactured by Tokushu Kika Kogyo Co., Ltd., trade name: T.K. Homojetter, Model M) over about 3 minutes, to conduct the neutralization reaction. Stirring was continued for 15 minutes after the addition to obtain an aluminum hydroxide slurry. During the neutralization reaction, an ultimate temperature was 15°C .

[0054] The aluminum hydroxide slurry thus obtained was centrifuged to recover only a solid content, and the step of suspending the solid content in 2 liter of deionized water, followed by solid-phase separation, was repeated seven times. Then, the resultant was washed with deionized water (total amount of about 14 liter). The wet cake after washing was dispersed in water again to adjust to a cake concentration to 6%, and then dried by Spray dryer (manufactured by Niro A/S, trade name: Mobile minor type) under the conditions of a drying temperature of 250°C (dryer inlet temperature) and 100°C (dryer outlet temperature) and an atomizer pressure of $1.2 \text{ kg}/\text{cm}^2$ to obtain an aluminum hydroxide powder. Powder physical properties of the resulting aluminum hydroxide powder are shown in Table 1.

Example 2

[0055] According to the same manner as that described in Example 1 except for changing the raw materials used for neutralization to 533 ml of a sodium aluminate solution (sodium concentration: 125 g/l in terms of Na_2O , molar ratio $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 : 1.55$) and 880 ml of an aqueous aluminum sulfate solution (aluminum concentration: 3.2% by weight in terms of Al_2O_3), an aluminum hydroxide powder was obtained. Powder physical properties of the resulting aluminum hydroxide powder are shown in Table 1.

Example 3

[0056] An aluminum hydroxide slurry was obtained in the same manner as in Example 1, except that the stirring was conducted under the conditions of the shear rate of 11000 sec^{-1} for 15 minutes after the neutralization reaction, followed by stirring under the conditions of the shear rate of 3300 sec^{-1} for additional 2 hours to conduct aging. The temperature after aging was 8°C . The resulting aluminum hydroxide slurry was washed and then dried according to the same manner as that described in Example 1 to obtain an aluminum hydroxide powder. Powder physical properties of the resulting aluminum hydroxide powder are shown in Table 1.

Example 4

(Preparation of rubber composition containing aluminum hydroxide)

5 [0057] 137.5 Parts by weight of SBR (styrene content/vinyl unit content in butadiene = 30/50 (wt%/%), Aroma-oil: 37.5 parts by weight, Mooney viscosity ML_{1+4} 100°C: 55, solution polymerized styrene-butadiene rubber containing about 60% by weight of branched moiety which is attributed to $SiCl_4$ added at the time of producing), 78.4 parts by weight of an aluminum hydroxide (each one obtained in Examples 1 to 3), 10.1 parts by weight of an Aroma-oil (manufactured by Kyodo Sekiyu Co., Ltd., trade name: X-140) and 12.8 parts by weight of a silane coupling agent (manufactured by Degussa AG, trade name: X-505) were introduced in a Labo plastomill (manufactured by Toyo Seiki Seisakusho Co., Ltd., type: 30-C150, mixer type: B-75) whose temperature has previously been set to 110°C, in this order, and kneaded at a blade revolution of 80 rpm for 3 minutes. After the blade revolution was raised to 100 rpm, the mixture was further kneaded for 2 minutes to obtain a rubber composition containing an aluminum hydroxide.

10 [0058] The composition was vulcanized at 160°C for 45 minutes and physical properties of the resulting vulcanized product were measured. The results are shown in Table 1.

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Comparative Example 1

20 [0059] According to the same manner as that described in Example 4 except for using White Carbon (manufactured by Degussa Co., trade name: Ultrasil VN3 GR) in place of the aluminum hydroxide, a composition comprising the rubber and White Carbon was obtained.

[0060] The composition was vulcanized at 160°C for 45 minutes and physical properties of the resulting vulcanized product were measured. The results are shown in Table 1.

25 Comparative Example 2

30 [0061] According to the same manner as that described in Example 4 except for using a commercially available aluminum hydroxide (manufactured by Sumitomo Chemical Industries Co., Ltd., trade name: C-301) as the aluminum hydroxide in case of preparing the rubber composition containing the aluminum hydroxide, a rubber composition containing an aluminum hydroxide was obtained. The composition was vulcanized at 160°C for 45 minutes and physical properties of the resulting vulcanized product were measured. The results are shown in Table 1.

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		Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2
5 10 15 20 25 30	Powder physical properties	BET specific surface area (m ² /g) 60	250	95	170	5
		Maximum value in pore size distribution (nm) 30	12	14	25	300
		Mean particle size of secondary particles (μ) 1.9	2.5	1.3	-	1.0
35	Vulcanized product physical properties	Grip performance 50	32	41	100	90
		Rolling resistance 47	53	56	100	59
		Processability 51	59	54	100	52

Claims

1. An aluminum hydroxide wherein the mean particle size of the secondary particles is from 0.1 to 8 μm, the BET specific surface area is not less than about 30 m²/g and the pore size distribution has a maximum value within the range from 5 to 100 nm.
2. An aluminum hydroxide according to claim 1, wherein the BET specific surface area is not more than 500 m²/g.
3. An aluminum hydroxide according to claim 1 or 2, wherein the mean particle size of the primary particles is from 10 to 100 nm.
4. An aluminum hydroxide according to any one of claims 1 to 3, which has been subjected to a surface treatment.
5. An aluminum hydroxide according to any one of claims 1 to 4, which has been subjected to a drying step.
6. An aluminum hydroxide according to claim 1, obtained by carrying out a neutralization reaction by mixing a basic solution and an acidic solution, one or both of the solutions containing an aluminum ion, under high-speed rotary shear stirring which produces a shear rate of not less than 1000 sec⁻¹, and separating the resulting neutralization reaction product, followed by drying.
7. A method for producing an aluminum hydroxide wherein the mean particle size of the secondary particles is from 0.1 to 8 μm, the BET specific surface area is not less than about 30 m²/g and the pore size distribution has a maximum value within the range from 5 to 100 nm, which comprises carrying out a neutralization reaction by mixing

a basic solution and an acidic solution, one or both of the solutions containing an aluminum ion, under high-speed rotary shear stirring which produces a shear rate of not less than 1000 sec⁻¹, and separating the resulting neutralization reaction product, followed by drying using a flash dryer, a hot-air transfer type dryer or a vacuum dryer.

- 5 8. A method according to claim 7, wherein the neutralization reaction product is washed prior to drying.
9. A method according to claim 7 or 8, wherein the basic solution is an aqueous solution of an alkali metal aluminate, sodium hydroxide, potassium hydroxide or ammonia.
10. A method according to any one of claims 7 to 9, wherein the acidic solution is an aqueous solution of aluminum sulfate, sulfuric acid, hydrochloric acid or acetic acid.
11. A method according to any one of claims 7 to 10, wherein the mixing under high-speed rotary shear stirring is carried out in the presence of a water-soluble polymer.
- 15 12. A method according to any one of claims 7 to 11, wherein the mixing under high-speed rotary shear stirring is carried out at a temperature within the range from 0 to 50°C.
13. A method according to any one of claims 7 to 12, which comprises aging the neutralization reaction product.
- 20 14. A method according to any one of claims 7 to 13, which comprises subjecting the neutralization reaction product to a grinding treatment at any stage from the mixing under high-speed rotary shear mixing to the drying.
- 25 15. Use of an aluminum hydroxide wherein the mean particle size of the secondary particles is from 0.1 to 8 µm, the BET specific surface area is not less than about 30 m²/g and the pore size distribution has a maximum value within the range from 5 to 100 nm in a rubber composition.
16. Use according to claim 15, wherein the aluminum hydroxide is used as a filler in a rubber composition for tire tread.
- 30 17. Use according to claim 15 or 16, wherein the aluminum hydroxide is present in a proportion of 10 to 200 parts by weight based on 100 parts by weight of the rubber component.
- 35 18. A rubber composition for tire tread, comprising a rubber component and an aluminum hydroxide wherein the mean particle size of the secondary particles is from 0.1 to 8 µm, the BET specific surface area is not less than about 30 m²/g and the pore size distribution has a maximum value within the range from 5 to 100 nm, the aluminum hydroxide being present in the composition in a proportion of 10 to 200 parts by weight based on 100 parts by weight of the rubber component.
- 40 19. A tire having a tread comprising a rubber component and an aluminum hydroxide according to any one of claims 1 to 5.

Patentansprüche

- 45 1. Aluminiumhydroxid, wobei die mittlere Teilchengröße der Sekundärteilchen 0,1 bis 8 µm beträgt, die spezifische Oberfläche nach BET nicht weniger als etwa 30 m²/g beträgt und die Porengrößenverteilung einen Maximalwert im Bereich von 5 bis 100 nm aufweist.
2. Aluminiumhydroxid nach Anspruch 1, wobei die spezifische Oberfläche nach BET nicht mehr als 500 m²/g beträgt.
- 50 3. Aluminiumhydroxid nach Anspruch 1 oder 2, wobei die mittlere Teilchengröße der Primärteilchen 10 bis 100 nm beträgt.
4. Aluminiumhydroxid nach einem der Ansprüche 1 bis 3, das einer Oberflächenbehandlung unterzogen wurde.
- 55 5. Aluminiumhydroxid nach einem der Ansprüche 1 bis 4, das einer Trocknungsstufe unterzogen wurde.
6. Aluminiumhydroxid nach Anspruch 1, das durch Durchführen einer Neutralisationsreaktion durch Vermischen einer

basischen Lösung und einer sauren Lösung, wobei eine oder beide der Lösungen Aluminiumionen enthalten, unter Schnellrotationsscherröhren, wobei eine Scherrate von nicht weniger als 1000 s^{-1} erreicht wird, und Abtrennen des gebildeten Neutralisationsreaktionsprodukts und anschließendes Trocknen erhalten wurde.

5 7. Verfahren zur Herstellung eines Aluminiumhydroxids, wobei die mittlere Teilchengröße der Sekundärteilchen 0,1 bis 8 μm beträgt, die spezifische Oberfläche nach BET nicht weniger als etwa $30\text{ m}^2/\text{g}$ beträgt und die Porengrößenverteilung einen Maximalwert im Bereich von 5 bis 100 nm aufweist, das das Durchführen einer Neutralisationsreaktion durch Vermischen einer basischen Lösung und einer sauren Lösung, wobei eine oder beide der Lösungen Aluminiumionen enthalten, unter Schnellrotationsscherröhren, wobei eine Scherrate von nicht weniger als 1000 s^{-1} erreicht wird, und Abtrennen des gebildeten Neutralisationsreaktionsprodukts und anschließendes Trocknen unter Verwendung eines Schnelltrockners, Heißlufttrockners vom Übertragungstyp oder Vakuumtrockners umfasst.

10 8. Verfahren nach Anspruch 7, wobei das Neutralisationsreaktionsprodukt vor dem Trocknen gewaschen wird.

15 9. Verfahren nach Anspruch 7 oder 8, wobei die basische Lösung eine wässrige Lösung eines Alkalimetallaluminats, von Natriumhydroxid, Kaliumhydroxid oder Ammoniak ist.

20 10. Verfahren nach einem der Ansprüche 7 bis 9, wobei die saure Lösung eine wässrige Lösung von Aluminiumsulfat, Schwefelsäure, Salzsäure oder Essigsäure ist.

25 11. Verfahren nach einem der Ansprüche 7 bis 10, wobei das Mischen unter Schnellrotationsscherröhren in Gegenwart eines wasserlöslichen Polymers durchgeführt wird.

30 12. Verfahren nach einem der Ansprüche 7 bis 11, wobei das Mischen unter Schnellrotationsscherröhren bei einer Temperatur im Bereich von 0 bis 50 °C durchgeführt wird.

35 13. Verfahren nach einem der Ansprüche 7 bis 12, das eine Nachbehandlung des Neutralisationsreaktionsprodukts umfasst.

40 14. Verfahren nach einem der Ansprüche 7 bis 13, das das Durchführen einer Mahlbehandlung an dem Neutralisationsreaktionsprodukt in einer beliebigen Stufe vom Mischen unter Schnellrotationsschermischen bis zum Trocknen umfasst.

45 15. Verwendung eines Aluminiumhydroxids, wobei die mittlere Teilchengröße der Sekundärteilchen 0,1 bis 8 μm beträgt, die spezifische Oberfläche nach BET nicht weniger als etwa $30\text{ m}^2/\text{g}$ beträgt und die Porengrößenverteilung einen Maximalwert im Bereich von 5 bis 100 nm aufweist, in einer Kautschukzusammensetzung.

50 16. Verwendung nach Anspruch 15, wobei das Aluminiumhydroxid als Füllstoff in einer Kautschukzusammensetzung für eine Reifenlauffläche verwendet wird.

55 17. Verwendung nach Anspruch 15 oder 16, wobei das Aluminiumhydroxid in einem Verhältnis von 10 bis 200 Gewichtsteilen, bezogen auf 100 Gewichtsteile der Kautschukkomponente, vorhanden ist.

60 18. Kautschukzusammensetzung für eine Reifenlauffläche, die eine Kautschukkomponente und ein Aluminiumhydroxid, wobei die mittlere Teilchengröße der Sekundärteilchen 0,1 bis 8 μm beträgt, die spezifische Oberfläche nach BET nicht weniger als etwa $30\text{ m}^2/\text{g}$ beträgt und die Porengrößenverteilung einen Maximalwert im Bereich von 5 bis 100 nm aufweist, umfasst, wobei das Aluminiumhydroxid in der Zusammensetzung in einem Verhältnis von 10 bis 200 Gewichtsteilen, bezogen auf 100 Gewichtsteile der Kautschukkomponente, vorhanden ist.

65 19. Reifen, der eine Lauffläche aufweist, die eine Kautschukkomponente und ein Aluminiumhydroxid gemäß einem der Ansprüche 1 bis 5 umfasst.

55 **Revendications**

1. Hydroxyde d'aluminium dans lequel la taille moyenne de particule des particules secondaires est comprise entre 0,1 μm et 8 μm , la surface spécifique BET n'est pas inférieure à environ $30\text{ m}^2/\text{g}$ et la distribution de taille de pore

a une valeur maximum comprise dans une plage allant de 5 nm à 100 nm.

2. Hydroxyde d'aluminium selon la revendication 1, dans lequel la surface spécifique BET n'est pas supérieure à 500 m²/g.

5 3. Hydroxyde d'aluminium selon la revendication 1 ou la revendication 2, dans lequel la taille moyenne de particule des particules primaires est comprise entre 10 nm et 100 nm.

10 4. Hydroxyde d'aluminium selon l'une quelconque des revendications 1 à 3, qui a été soumis à un traitement de surface.

5 5. Hydroxyde d'aluminium selon l'une quelconque des revendications 1 à 4, qui a été soumis à une étape de séchage.

15 6. Hydroxyde d'aluminium selon la revendication 1, obtenu en effectuant une réaction de neutralisation par mélangeage d'une solution basique et d'une solution acide, une des deux solutions contenant un ion aluminium, sous agitation à cisaillement rotatif grande vitesse laquelle produit un taux de cisaillement qui n'est pas inférieur à 1000 s⁻¹, et en séparant le produit de la réaction de neutralisation qui en résulte, suivi d'un séchage.

20 7. Procédé pour produire un hydroxyde d'aluminium dans lequel la taille moyenne de particule des particules secondaires est comprise entre 0,1 µm et 8 µm, la surface spécifique BET n'est pas inférieure à environ 30 m²/g et la distribution de taille de pore a une valeur maximum comprise dans une plage allant de 5 nm à 100 nm, qui comprend l'exécution d'une réaction de neutralisation par mélangeage d'une solution basique et d'une solution acide, une des deux solutions contenant un ion aluminium, sous agitation à cisaillement rotatif grande vitesse laquelle produit un taux de cisaillement qui n'est pas inférieur à 1000 s⁻¹, et la séparation du produit de la réaction de neutralisation qui en résulte, suivi par un séchage en utilisant un séchoir-éclair, un séchoir à transfert d'air chaud ou un sécheur sous vide.

25 8. Procédé selon la revendication 7, dans lequel le produit de la réaction de neutralisation est lavé avant séchage.

30 9. Procédé selon la revendication 7 ou la revendication 8, dans lequel la solution basique est une solution aqueuse d'un aluminate de métal alcalin, d'hydroxyde de sodium, d'hydroxyde de potassium ou d'ammoniac.

35 10. Procédé selon l'une quelconque des revendications 7 à 9, dans lequel la solution acide est une solution aqueuse de sulfate d'ammonium, d'acide sulfurique, d'acide chlorhydrique ou d'acide acétique.

11. Procédé selon l'une quelconque des revendications 7 à 10, dans lequel le mélangeage sous agitation à cisaillement rotatif grande vitesse est effectué en présence d'un polymère soluble dans l'eau.

40 12. Procédé selon l'une quelconque des revendications 7 à 11, dans lequel le mélangeage sous agitation à cisaillement rotatif grande vitesse est effectué à une température comprise dans la plage allant de 0 °C à 50 °C.

13. Procédé selon l'une quelconque des revendications 7 à 12, qui comprend le vieillissement du produit de la réaction de neutralisation.

45 14. Procédé selon l'une quelconque des revendications 7 à 13, qui comprend la soumission du produit de la réaction de neutralisation à un traitement de broyage à n'importe quel stade du mélangeage sous agitation à cisaillement rotatif grande vitesse jusqu'au séchage.

50 15. Utilisation dans une composition de caoutchouc d'un hydroxyde d'aluminium dans lequel la taille moyenne de particule des particules secondaires est comprise entre 0,1 µm et 8 µm, la surface spécifique BET n'est pas inférieure à environ 30 m²/g et la distribution de taille de pore a une valeur maximum comprise dans une plage allant de 5 nm à 100 nm.

55 16. Utilisation selon la revendication 15, dans laquelle l'hydroxyde d'aluminium est utilisé en tant que charge dans une composition de caoutchouc pour bande de roulement de pneumatique.

17. Utilisation selon la revendication 15 ou la revendication 16, dans laquelle l'hydroxyde d'aluminium est présent dans une proportion de 10 parts à 200 parts en poids pour 100 parts du composant caoutchouc.

18. Composition de caoutchouc pour bande de roulement de pneumatique, comprenant un composant caoutchouc et un hydroxyde d'aluminium dans lequel la taille moyenne de particule des particules secondaires est comprise entre 0,1 µm et 8 µm, la surface spécifique BET n'est pas inférieure à environ 30 m²/g et la distribution de taille de pore a une valeur maximum comprise dans une plage allant de 5 nm à 100 nm, l'hydroxyde d'aluminium étant présent dans la composition dans une proportion de 10 parts à 200 parts en poids pour 100 parts en poids du composant caoutchouc.

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19. Pneumatique ayant une bande de roulement comprenant un composant et un hydroxyde d'aluminium selon l'une quelconque des revendications 1 à 5.

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